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PLASMA-SPRAYED ELECTRICALLY INSULATING CERAMIC COATINGS

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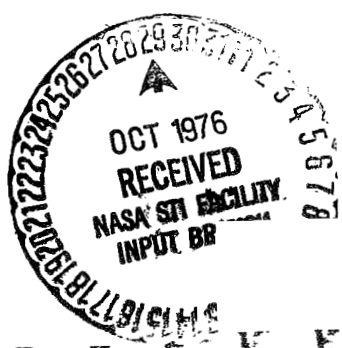

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16. Abstract
The technique of plasma spraying makes possible the deposition of electrically insulating ceramic coatings on metals, graphite and other conductors. The oxide ceramic materials usable for this purpose are described and the range of possible applications is illustrated by a number of examples. The chief advantages of the coatings are: 1. electrical insulation even at high temperatures, 2. electrical insulation combined with good thermal conductivity, 3. independence of the shape of the body to be insulated, 4. possibility of local insulation.

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Plasma-Sprayed Electrically Insulating Ceramic Coatings

K. Kirner

1. Introduction

/220*

Ceramics have long been used for electrical insulation. They are usually prepared by sintering. Only simple shapes can be obtained with this technique. Moreover, there are difficulties in attaching the ceramic to metal, since ceramics are brittle -- and thus cannot be riveted or screwed on conveniently -- and since soldering is only possible after special treatments.

Most oxide insulator ceramics melt at very high temperatures; hence it is rarely possible to apply coatings in molten ceramic.

Plasma-spraying technology, with its high temperatures, offers new opportunities and extends ceramic technology in the same way as it did the technology of refractory metallic materials [1, 2]. Of course the new techniques do not eliminate all the restrictions associated with the use of ceramics; the examples to be described later will indicate the scope of applications for sprayed ceramic insulating coatings.

Sprayed ceramic coatings have other favorable properties as well, such as extreme hardness, good resistance to wear, and in some cases favorable absorption/emission characteristics [3], which result in further possible applications.

*Numbers in the margin indicate pagination in the foreign text.

2. Oxide Ceramic Insulators Suitable for Plasma Spraying

Virtually all electrically insulating metal oxides can be plasma-sprayed. The oxide coatings employed in practice, usually to combat wear or influence thermal conduction, have been almost exclusively aluminum oxide (Al_2O_3) and zirconium oxide (ZrO_2).

The oxide material required for a specific purpose will be selected primarily on the basis of its physical and technological properties: another important parameter is price. Table 1 shows the important oxide ceramic materials with a number of important properties. The values refer to massive sintered objects. Very little numerical data is available for sprayed ceramic coatings: since these sprayed coatings are always porous to some extent -- unless subjected to further treatment -- some of the technological properties, such as strength, hardness, and thermal conduction, will not be as good as for dense sintered objects. Table 2 shows the hardnesses of sprayed ceramic coatings.

The characteristic feature of sprayed coatings is the laminar structure, caused by the spattering of the liquid ceramic particles upon impact. Plasma-spraying has been done almost exclusively /221 with powder. Fine powders -- that is, with grain sizes around 25 μm -- yield denser sprayed structures than coarser powders, and the coatings sprayed with fine powder can be polished better. There is a lower bound on the grain size of the ceramic spraying powder determined by its pourability; there is also an upper bound determined by the output of the plasma torch, so that the usable range of grain diameter extends from about 20 to 70 μm. However, in order to match grain size to torch output, it is best to have a finer classification, e.g. 25 $\pm$ 5 μm.

For some of the oxides listed in Table 1, there are several phases for a given chemical composition, i.e. these oxides are allotropic, such as Al_2O_3, titanium dioxide (TiO_2), silicon dioxide

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TABLE 1. PROPERTIES OF OXIDE CERAMIC MATERIALS

Stoff a	Spez. Gewicht [g/cm³] b	Schmelzpunkt [°C] c	Härte [kp/mm²] (und Mohs) d	elektrischer Widerstand [Ω·cm] e	Wärmeleitung [cal/cm·°C·s] f	Wärmeausdehnung je °C·10⁻⁶ g	Bemerkungen h	
Al_2O_3	3,98	2050	2000 bis 3000 HV (9 Mohs)	10^{14} (25°)	0,10 (38°) 0,018 (700°)	8,0	hohe Festigkeit, hart, verschleißfest, gutes Dielektrikum, billig	l
BeO	3,02	2550	750 bis 1500 HV	10^{17} (20°) 10^{13} (260°) 10^{6} (1100°)	0,53 (20°)	9,5	ausgezeichnete Wärmeleitfähigkeit, gute Wärmeschockbeständigkeit, giftig	m
CaO	3,4	2560	(4½ Mohs)	10^{8} (760°) 10^{3} (1500°)	0,032 (20°)	13,6	nur wenn dicht gesintert, wasserfest, sonst Auflösung	n
Cr_2O_3	5,21	2265	etwa 2000 HV	10^{2} (350°) 10^{2} (760°)	0,15 (38°) 0,03 (700°)	8,4	hart, verschleißfest, hohe Oberflächengüte, gute Wärmeleitfähigkeit	o
MgO	3,58	2800	370 HKn (5½ Mohs)	10^{5} (950°)	0,08 (20°)	14	hoher Schmelzpunkt, hohe Wärmeausdehnung	p
SiO_2	2,32	1710	(7 Mohs)	bis 10^{18}	0,003 (20°)	0,5	geringe Wärmeleitfähigkeit, geringe Wärmedehnung, einzigartige Wärmeschockbeständigkeit, hoher elektrischer Widerstand	q
TiO_2	4,24 (Rutil)	1950	(6 bis 7½ Mohs)	10^{7} (500°) 10^{4} (800°)	0,023 (38°) 0,009 (700°)	8,6	sehr gutes Dielektrikum	r
ZrO_2 rein i	6,1	2677	1200 HKn (7 Mohs)	10^{6} (385°) 10^{4} (700°) 10^{2} (1200°)	0,004 (38°) 0,0043 (700°)	7,4	gute Wärmedämmung, bei höheren Temperaturen guter elektrischer Leiter	s
ZrO_2 stab. j mit 5% CaO	5,6	2550	700 bis 900 HV (6½ Mohs)	–	0,02 (20°)	9,4		
$BaTiO_3$	6,01	1610	–	–	0,0062 (20°)	9	gutes Dielektrikum, leicht schleifbar	t
Porzellan k	2,3 bis 2,5	≈ 1600	–	10^{11}	0,002 (20°)	4,5	billig	u

Compiled from figures in the literature; from this data, which varies widely, we give the most probable values.

Key: bis = to
etwa = about

a. Material
b. Specific gravity
c. Melting point
d. Hardness
e. Electrical resistivity
f. Thermal conductivity
g. Thermal expansion
h. Remarks
i. Pure
j. Stabilized with
k. Porcelain

l. High strength, hardness, wear-resistant, good dielectric, inexpensive
m. Excellent thermal conductivity, good thermal-shock resistance, toxic
n. Insoluble in water only when densely sintered
o. Hard, wear-resistant, high surface quality, good thermal conductivity
p. High melting point, high thermal expansion

[Key continued]

q. Low thermal conductivity, low thermal expansion, unique thermal-shock resistance, high electrical resistivity
r. Very good dialectric
s. Good thermal insulator, good electrical conductor at high temperatures
t. Good dialectric, easily ground
u. Inexpensive

TABLE 2. HARDNESS OF SPRAYED CERAMIC COATINGS

Stoff a	Zustand b	Härte HV [kp/mm²] Mittelwerte c
Al_2O_3	gespritzt	etwa 1000
	gespritzt und geglüht	etwa 1500
Al_2O_3 + 3% TiO_2	gespritzt mit d normalem Abstand	1030 bis 1130
	gespritzt mit kurzem Abstand e	etwa 2000
KM 31-Mass	gespritzt	etwa 1250
Cr_2O_3	gespritzt	1250 bis 1470
TiO_2	gespritzt	etwa 850
$BaTiO_3$	gespritzt	etwa 730
	gespritzt und geglüht	etwa 1650
ZrO_2 + 10% CaO	gespritzt	etwa 700

Key: gespritzt = sprayed
geglüht = annealed
a. Material
b. State
c. Average hardness HV 0.1 [kg/mm^2]
d. Sprayed at normal distance
e. Sprayed at short distance
etwa = about
bis = to

(SiO_2), and ZrO_2. When sprayed, these substances can therefore undergo phase transformations, and it may happen that unstable states will be "frozen in," since the coatings cool extremely rapidly. Al_2O_3 coatings sprayed with powder in the refractory, hexagonal α-phase essentially consists of cubic γ-Al_2O_3. When /222

annealed above 1000°C, this γ-Al_2O_3 is converted back to the α-Al_2O_3. Often oxygen will be lost from the oxides in passing through the extremely hot plasma zones; for instance, the sprayed material may only be $TiO_{1.98}$ instead of TiO_2. This alters the appearance -- TiO_2 rutile is yellowish white, but $TiO_{1.98}$ is black -- and the unoccupied lattice sites (the holes) can reduce the electrical resistivity somewhat; in most cases, it will still be quite adequate for insulation purposes.

3. Applications of Plasma-Sprayed Oxide Insulating Coatings

3.1. Insulating Coatings for Electrolytic Machines

In electrolytic deburring machines, the rotating electrode-shafts must be insulated from the housing, since there is a low electrical potential between them. There are also certain temperature-stability and corrosion-resistance requirements. One feasible idea has proven to be using plasma-sprayed oxide bearing seats on the shafts. The shafts are lathed about 0.25 mm thinner at these bearing points, and a 0.5 mm coating of Al_2O_3 or barium titanate ($BaTiO_3$) plasma sprayed at these points. The coating is then ground to the desired dimensions. Roller bearings are then moved into place over the seats. We have coated stainless steel (Fig. 1) and brass shafts by this method.

Likewise for these electrolytic deburring machines, electrodes have been locally insulated with plasma-sprayed ceramic coatings (Fig. 2).

3.2. Electrical Insulation for Heat Sinks in Electronics Packaging

When packed closely together, electronic components can lose enough heat to raise the temperature of the package to unacceptable levels. Therefore, heat must be bled off from the electronics components: however, the parts must be electrically insulated.

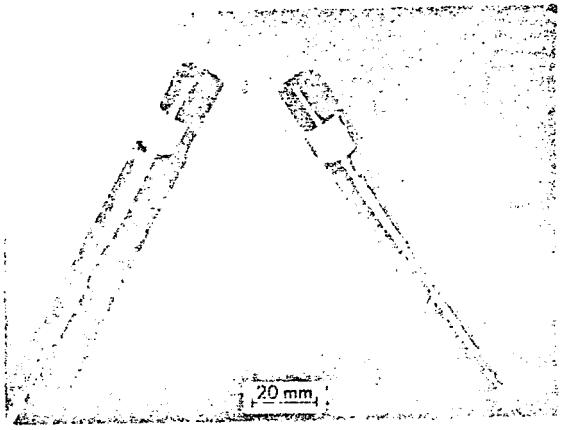

Fig. 1. Shafts of stainless steel with plasma-coated ceramic insulating rings.

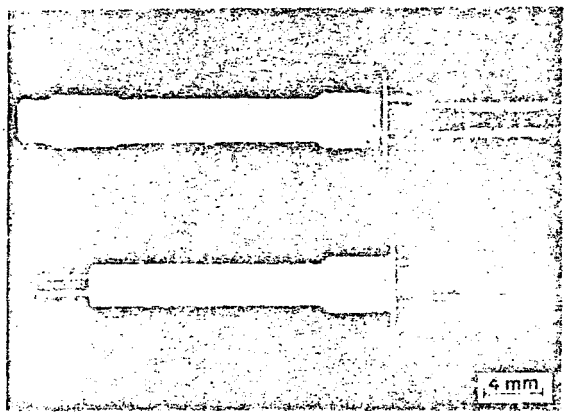

Fig. 2. For electrolytic deburring with plasma-sprayed Al_2O_3 insulation.

One solution is to use as heat sinks plates of sufficient mass equipped with cooling ribs. Another is to use the mass of the fasteners to absorb and distribute heat.

Table 1 shows that beryllium oxide (BeO) has an extraordinarily high thermal conductivity (only a few metals such as gold, silver, and copper conduct heat better) and that it is likewise a good electrical insulator. Unfortunately, however, BeO is highly toxic (maximum place-of-work concentration 2 mg/m^3) and cannot be worked with without special safety measures; it is therefore not feasible as a spraying material in general. Chromium oxide (Cr_2O_3) and Al_2O_3 likewise have relatively good thermal conductivities and are good electrical insulators, Al_2O_3 even a very good one.

On aluminum heat-removal plates for 400 A and 500 A rectifier boxes, we sprayed Al_2O_3 and ZrO_2 and substantially improved heat removal over that obtained with organic insulators. Fig. 3 shows such cooling plates with plasma-sprayed Al_2O_3 coatings. We measured the following thermal conductivities (determined by Peter Storz, Robert Bosch GmbH, Stuttgart 1968):

for sprayed Al_2O_3:

λ = 3.9 W/m/°C ≃ 0.01 cal/cm/°C/sec.

for sprayed ZrO_2:

λ = 1.23 W/m/°C ≃ 0.003 cal/cm/°C/sec.

(by comparison: Hostaphan:

λ = 0.13 W/m/°C ≃ 0.0003 cal/cm/°C/sec.

Epoxide resin: /223

λ = 0.22 W/m/°C ≃ 0.0005 cal/cm/°C/sec)

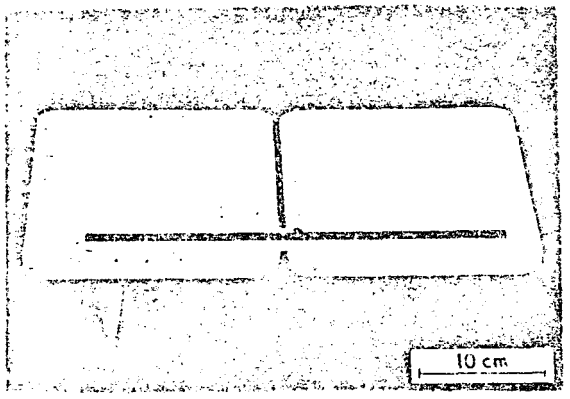

Fig. 3. Cooling plates with electrically insulating but thermally conducting Al_2O_3 plasma-sprayed coatings (with 30 cm scale).

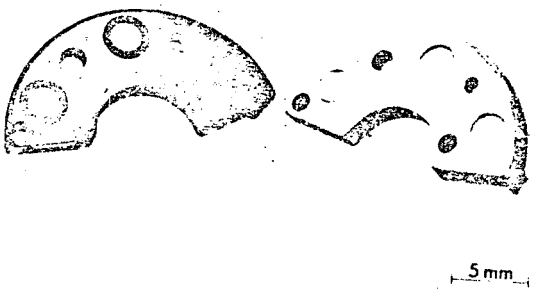

Fig. 4. Diode plates with electrically insulating thermally conducting plasma-sprayed and polished ceramic coatings. Left: Cr_2O_3. Right: Al_2O_3.

The following values were obtained in the US:

for plasma-sprayed Al_2O_3:

λ = 0.05 cal/cm/°C/sec.

for plasma-sprayed BeO:

λ = 0.4 cal/cm/°C/sec [4].

Fig. 4 shows two plates with three packaged diodes each. One plate has a polished Al_2O_3 plasma-sprayed coating, and the other a Cr_2O_3 coating.

Fig. 5 shows that very tiny surfaces can be given an oxide coating, and that other materials, such as solderable metals, can then be sprayed on the ceramic substrate.

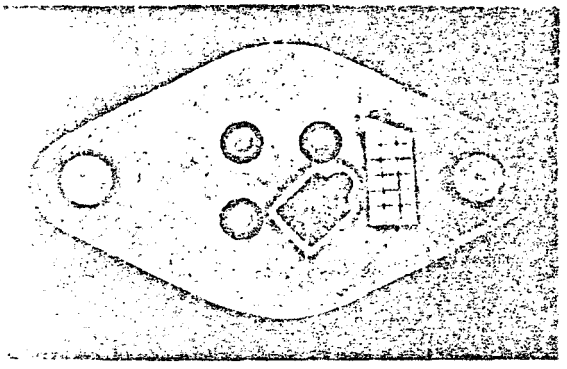

Fig. 5. Piece of metal with a small plasma-sprayed ceramic insulator coating with a nickel layer sprayed onto it. (A piece of millimeter-scale paper is shown as a size comparsion)

3.3. High-temperature Insulting Coatings

In the case of organic insulators, the operating temperature must generally be less than about 200 °C. Only inorganic insulators, such as mica, ceramics and glass, can withstand higher temperatures. Oxide ceramic coatings offer numerous possible applications for parts exposed to high temperatures, since no special consideration must be paid to the thickness and shape of the parts. Oxide ceramic coatings can be sprayed in thicknesses from less than 0.1 mm to several millimeters.

Fig. 6 shows Hall generator parts onto which are sprayed 0.2-0.4 mm Al_2O_3 coatings as electrical insulation. These Al_2O_3 coatings can be used up to a maximum of 1000 °C. Around 1000 °C, there is a phase transformation, the γ-form of Al_2O_3 being converted to the α-modification, and this is associated with a decrease in volume; the shrinkage can cause the sprayed coating to split.

This transformation plays a less important role when thin "self-bearing" shaped parts of Al_2O_3 can be fabricated by spraying, as in the case of the heating conductor supports shown in Fig. 7. These thin ceramics are produced by spraying onto brass cores, in

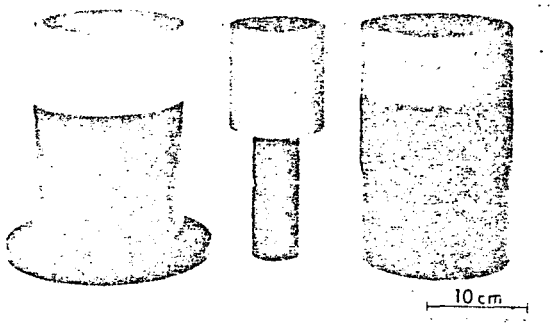

Fig. 6. Hall generator parts made of steel with plasma-sprayed Al_2O_3 ceramic coatings as electrical insulation for high temperatures.

which the pitch of the coil is grooved in the shape of a thread. /224 Once the desired thickness of about 0.1-0.2 mm or even more has been reached, the spraying process is terminated and the brass dissolved chemically. The sprayed coil sleeves can be dense-sintered and stabilized by annealing or even used without annealing; in the latter case, the first heating cycles will perform the stabilization.

The wire can be wound either on the outside or on the inside. The latter case is the one seen in Fig. 8: here a platinum wire coil is being heated to about 1500°C. Because the sleeves are so thin, the thermal inertia is very small, so that high heating frequencies are possible.

3.4. Ceramic Coated Wires

It is technically possible to spray ceramics onto wires made of copper, molybedenum, chrome nickel, and other materials. However, since the spraying beam is not tightly focused, having in fact a diameter of about 15-25 mm at a distance of 100 mm, spray coating wires, particularly thin wires, is inefficient and will be justified only in special cases. Wires with thin sprayed coatings (0.1 mm) can still be bent, but thicker layers will flake off when the wire is deformed. So far, we have coated wires up to 0,15 mm in diameter, with both Al_2O_3 and $BaTiO_3$. Spraying with other oxides should not present any difficulties.

A number of different materials can be sprayed in succession onto a given substrate, e.g. first $BaTiO_3$ and then Al_2O_3. This can

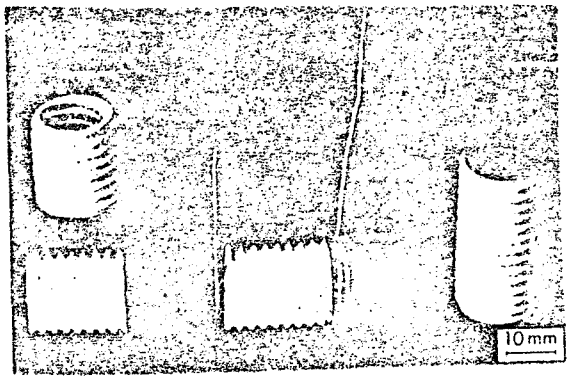

Fig. 7. Heating-conductor supports made of Al_2O_3 by plasma spraying.

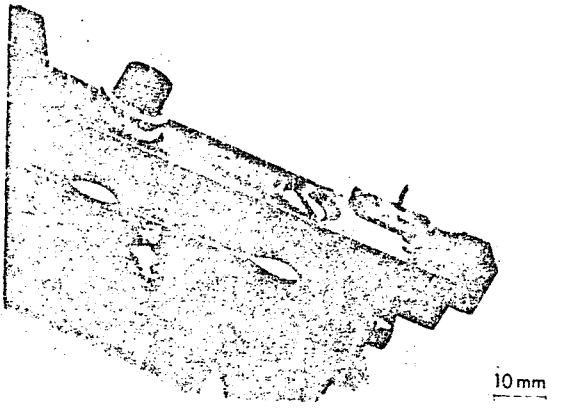

Fig. 8. Pt heating-conductor winding in plasma-sprayed Al_2O_3 supports, heated to 1500°C.

be useful in step-by-step matching of thermal expansion. The conductors copper and aluminum have large thermal expansion coefficients and ceramics have small ones. Thus, when the temperature varies, such composites can be subjected to considerable thermal stresses. Fig. 9 shows an example of multi-layer ceramic /225 coatings sprayed onto a copper wire 1 mm in diameter.

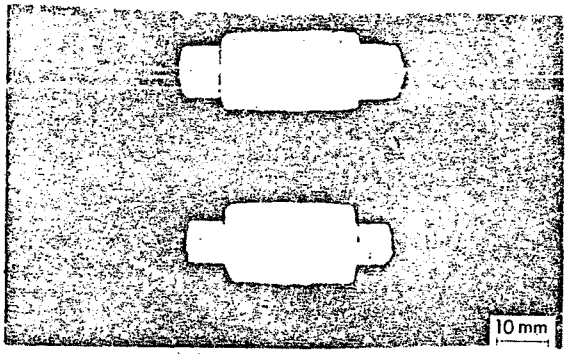

Fig. 9. Multi-layer ceramic coating sprayed onto a copper wire 1 mm in diameter; Al_2O_3 on the inside, $BaTiO_3$ on the outside.

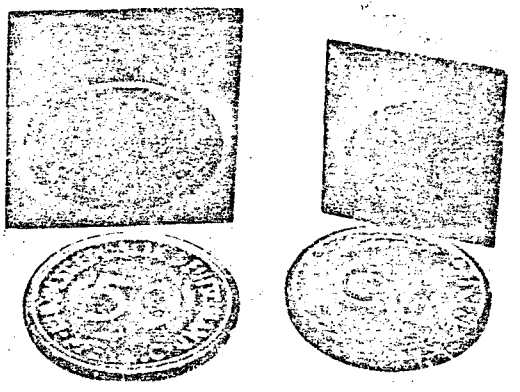

Fig. 10. Plasma-coated TiO_2 layers on Al. The TiO_2 coating is made mirror-smooth by grinding and polishing. Roughness depth 0.15 µm.

A gradual transition between two ceramic coatings (materials A and B) is also possible, beginning with pure ceramic A, continuing with a mixture of A and B, leading continuously from A to B, and then concluding with the pure ceramic B.

3.5. Sprayed Coatings with High Surface Quality

The surfaces of electrical insulators for which good cooling properties are desired must be as flat and smooth as possible, in order to maximize the area of contact. Thus the grinding and polishing properties of ceramic coatings are particularly important. Dense coatings such as $BaTiO_3$, TiO_2, and Cr_2O_3, can usually be worked to achieve a high surface finish. For instance, TiO_2 coatings polished with diamond paste and clay have a peak-to-valley height of 0.15-0.2 µm. As Fig. 10 shows, the surfaces are of mirror quality.

4. Metallographic Studies

While preparing metallographic sections of sprayed ceramic coatings on unrelated substrates is technically more difficult than for sprayed metal coatings on metal, it is nevertheless quite possible. The disks used for cutting should be diamond or at least silicon carbide (SiC). It will hardly be possible to prevent a few particles from breaking away from the sprayed coating during the cutting, so that the resulting surface will not be smooth as in the case of metals, but have a grainy structure like than shown in Fig. 11, which depicts a section through a coating -- sprayed with 25 µm Al_2O_3 powder on a steel substrate.

Hard ceramic coatings can then be cut and polished with diamond disks and diamond pastes. The laminar character of the coating will be particularly evident after polishing. This can readily be seen in Fig. 12 in the case of a Cr_2O_3 coating on steel.

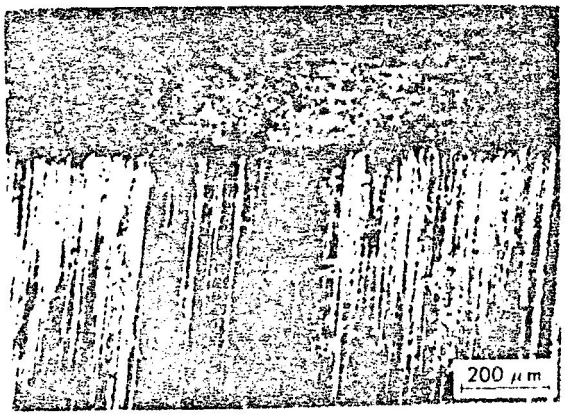

Fig. 11. Plasma-sprayed Al_2O_3 coating on steel after cutting with a SiC disk.

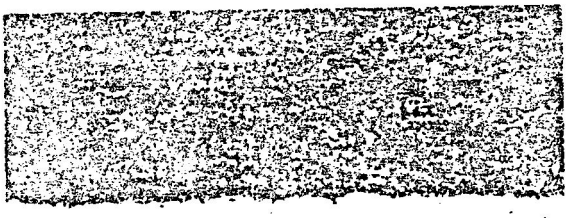

Fig. 12. Cross section through a plasma-sprayed Cr_2O_3 coating (top) on steel (bottom).

The sprayed Cr_2O_3 is black because of oxidation depletion. The bright lamellae in the coating are chromium. Incompletely oxidized particles are already present in the Cr_2O_3 powder as received. Moreover, the high temperatures in the plasma flame (argon plasma) promote a shift in the Cr_2O_3/Cr equilibrium in the direction of Cr.

In the case of plasma-sprayed ZrO_2 (Fig. 13), the laminar character of the layer can likewise be recognized due to oxygen concentration differences, although the differences are less distinct than in the case of Cr_2O_3. Several phases also exist for ZrO_2. Since the phase transformations result in major differences in thermal expansion coefficients, only stabilized ZrO_2 is used in practice, the cubic ZrO_2 phase being retained from room temperature up to the melting point due to the presence of calcium oxide (CaO) or oxides of the rare earths. During plasma spraying, almost half of the CaO stabilizer is lost; therefore in order to achieve satisfactory stabilization, the CaO content of the ZrO_2 starting powder must be higher than in ZrO_2 powder for sintering.

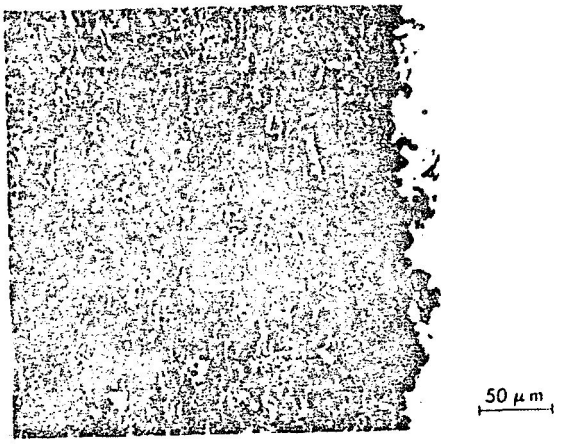

Fig. 13. Cross section through a plasma-sprayed ZrO_2 (left) on steel (right).

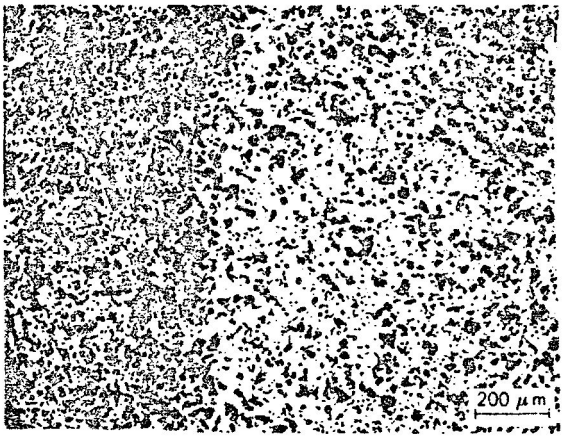

Fig. 14. Cross section through a sintered ceramic with a plasma-sprayed Al_2O_3 coating after annealing at 1600°C. Right: sintered ceramic. Left: sprayed ceramic.

The laminar character of the ceramic coatings vanishes when they are annealed above the recrystallization temperature, and a grainy structure is created, like that in ordinary sintered ceramics. Fig. 14 shows a section through an Al_2O_3 sprayed coating on a spark plug block. This specimen was annealed at 1600°C.

Such sintering both hardens (Table 2) and strengthens. /226 Since the sprayed ceramics are already rather dense, they do not shrink much (about 2% linear shrinkage), so that the dimensions remain nearly the same.

Of course free-standing ceramic objects can be annealed. Sprayed coatings on substrates can be annealed only when the substrate can withstand the high temperatures and when the differences in thermal expansion are small.

5. Prospects

We have discussed only the use of some simple oxides as plasma-sprayed insulating coatings. Since the development of this technology has just begun, however, there are still gaps in published information on the properties of

the materials. With increasing knowledge and experience, further possible applications will open up and an increasing amount of spraying will be done with mixed oxides and with mixtures of oxides and metals. Because they are very hard and resistant to wear, sprayed oxide coatings are particularly suitable for protecting parts against wear -- a field of great economic importance.

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